

AD-A111 153

FRANK J SEILER RESEARCH LAB UNITED STATES AIR FORCE A--ETC F/G 20/8  
MND0-ESTIMATIONS OF THE STANDARD ENTHALPY OF FORMATION OF SOME --ETC(U)  
FEB 82 S SENSARMA, A G TURNER, M J DELONG  
FJSRL-TR-82-0001

UNCLASSIFIED

NL

J-1  
A11153



END  
DATE  
FILMED  
3 82  
DTIC

(2)

LEVEL

II

(12)

FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT 82-0001

FEBRUARY 1982

MNDO-ESTIMATIONS OF THE STANDARD ENTHALPY  
OF FORMATION OF SOME BINARY SULFUR-NITROGEN  
COMPOUNDS AND THEIR DERIVATIVES

S. SENSARMA  
A. G. TURNER  
M. J. DELONG  
L. P. DAVIS

DTIC  
ELECTE  
S FEB 19 1982

B

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

PROJECT 2303

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

82 02 19 055 319 72

AD A111153



FJSRL-TR-82-0001

This document was prepared by the Molecular Dynamics Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit Number 2303-F4-03. Dr. Almon G. Turner was the project scientist.

When U. S. Government drawings, specifications or other data are used for any purpose other than a definitely related government procurement operation, the government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the government may have formulated, furnished or in any way supplied the said drawings, specifications or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

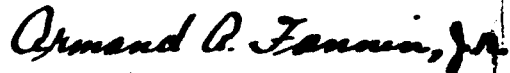
Inquiries concerning the technical content of this document should be addressed to the Frank J. Seiler Research Laboratory (AFSC), FJSRL/MC, USAF Academy, CO 80840. Phone AC 303 472-2655.

This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

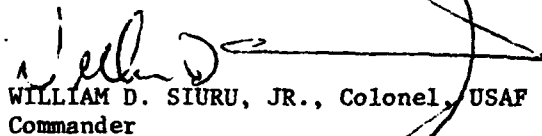
This technical report has been reviewed and is approved for publication.



ALMON G. TURNER, Ph.D.  
Project Scientist



ARMAND A. FANNIN, JR., Lt Colonel, USAF  
Director, Chemical Sciences



WILLIAM D. SIURU, JR., Colonel, USAF  
Commander

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Printed in the United States of America. Qualified requestors may obtain additional copies from the Defense Documentation Center. All others should apply to  
National Technical Information Service  
6285 Port Royal Road  
Springfield, Virginia 22161

MNDO-ESTIMATIONS OF THE STANDARD ENTHALPY OF FORMATION OF SOME  
BINARY SULFUR-NITROGEN COMPOUNDS AND THEIR DERIVATIVES

By

S. Sensarma<sup>†</sup>  
A. G. Turner<sup>†,\*</sup>  
M. J. DeLong  
L. P. Davis

TECHNICAL REPORT FJSRL-TR-82-0001

February 1982

Approved for public release; distribution unlimited

Directorate of Chemical Sciences  
Frank J. Seiler Research Laboratory  
Air Force Systems Command  
US Air Force Academy, Colorado 80840

<sup>†</sup> Permanent Address: Department of Chemistry, University of  
Detroit, Detroit, MI 48221

\* University Resident Research Professor, 1981-82. To whom  
correspondence should be addressed.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| REPORT DOCUMENTATION PAGE  |   | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM  |
|--|---|--|
| 1. REPORT NUMBER<br>FJSRL-TR-82-0001   | 2. GOVT ACCESSION NO.<br>ADA <b>111 153</b> | 3. RECIPIENT'S CATALOG NUMBER  |
| 4. TITLE (and Subtitle)<br>MNDO-Estimations of the Standard Enthalpy of Formation of Some Binary Sulfur-Nitrogen Compounds and Their Derivatives   |   | 5. TYPE OF REPORT & PERIOD COVERED   |
| 7. AUTHOR(s)<br>S. Sensarma            M. J. DeLong<br>A. G. Turner            L. P. Davis   |   | 6. PERFORMING ORG. REPORT NUMBER   |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>F. J. Seiler Research Laboratory (AFSC)<br>FJSRL/NC<br>USAF Academy, CO 80840   |   | 8. CONTRACT OR GRANT NUMBER(s)   |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>F. J. Seiler Research Laboratory (AFSC)<br>FJSRL/NC<br>USAF Academy, CO 80840   |   | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS<br><br>61102F/2303/F4/03 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)  |   | 12. REPORT DATE<br>February 1982   |
|  |   | 13. NUMBER OF PAGES  |
|  |   | 15. SECURITY CLASS. (of this report)<br><br>UNCLASSIFIED                             |
|  |   | 15a. DECLASSIFICATION DOWNGRADING SCHEDULE   |
| 16. DISTRIBUTION STATEMENT (of this Report)<br><br>Approved for public release; distribution unlimited.  |   |  |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)   |   |  |
| 18. SUPPLEMENTARY NOTES  |   |  |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Standard Enthalpy of Formation            Tetrasulfur tetranitride<br>Cyclic Sulfur Nitrides                      MNDO molecular orbital calculations<br>Sulfur Nitrides               |   |  |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br><br>A table of standard enthalpies of formation of all known binary compounds of sulfur and nitrogen has been compiled from a large number of MNDO type molecular orbital calculations. |   |  |

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

# TABLE OF CONTENTS

|  | <u>PAGE</u> |
|--|-------------|
| PREFACE . . . . .  | 11          |
| INTRODUCTION . . . . .   | 1           |
| CALCULATIONS AND RESULTS . . . . .   | 2           |
| TABLE OF THERMODYNAMIC DATA FOR VARIOUS SULFUR-<br>NITROGEN COMPOUNDS. . . . . | 4           |
| REFERENCES. . . . .  | 6           |



|                    |                                     |
|--------------------|-------------------------------------|
| Accession For      |                                     |
| DTIC               | <input checked="" type="checkbox"/> |
| DTIC               | <input type="checkbox"/>            |
| Unannounced        | <input type="checkbox"/>            |
| Justification      | <input type="checkbox"/>            |
| DTIC               |                                     |
| Availability Codes |                                     |
| Available and/or   |                                     |
| Dist. Special      |                                     |
| A                  |                                     |

## PREFACE

The research as herein described was performed under Work  
Unit 2303-F4-03 (Molecular Orbital Calculations of Excited Species).

## INTRODUCTION

The area of the chemistry of the binary molecules and ions formed from sulfur and nitrogen is of potential interest to the U. S. Air Force. Characterized by a dominance of highly endothermic compounds it offers a wide variety of materials for applications as primary solid state explosives and detonating agents. These materials are available in solid, liquid, and plastic forms. Representative compounds include tetranitrogen tetrasulfide,  $S_4N_4$ ; tetrasulfur dinitride,  $S_4N_2$  and the isomers thereof; and  $S_2N_2$ , disulfur dinitride. The latter compound can be readily converted into polymeric sulfur nitride,  $(SN)_x$ , which has been extensively studied for its electrical properties being a superconductor below 4K.

In addition to the above, the area of the binary compounds of sulfur and nitrogen contains a large number of polyhedral anions and cations. Representative members of this group include ions such as the tetrasulfur tetranitride dication,  $S_4N_4^{2+}$ ; tetrasulfur pentanitride anion,  $S_4N_5^{1-}$ ; tetrasulfur trinitride cation,  $S_4N_3^{1+}$ ; and trisulfur trinitride anion,  $S_3N_3^-$ . These anions and cations have potential application in the area of battery development as possible candidates for components of supporting electrolytes.

The area of the chemistry of binary compounds composed of sulfur and nitrogen has become a very active field of research in the last two decades<sup>1</sup>. Despite a wide range of research activities virtually no thermodynamic data are available for this class of materials, the exception being a single report of a value for the standard heat of formation of tetrasulfur tetrasulfur tetranitride<sup>2</sup>. Since our laboratory has been concerned with theoretical studies of these materials for a number of



years<sup>3</sup>, we have put together in tabular form estimates of the standard enthalpy of formation,  $\Delta H^\circ_f$  for most of the known compounds of this class. We have included a few materials which are presently unknown, (e.g.,  $N_2S$ ,  $S_4N_4^{2-}$ , and  $S_2N_2$  open chain) but whose existence may be considered probable, as reflected by the known chemistry of these materials<sup>4</sup>.

#### CALCULATION AND RESULTS

The enthalpies of formation have been calculated by the MNDO method of Dewar et.al.<sup>5</sup> using the Restricted Hartree-Fock approximation. Open shell systems have been calculated using an Unrestricted Hartree-Fock wave function<sup>6</sup>. The results are given in the Table.

The MNDO method when applied to sulfur-nitrogen compounds has been shown to predict molecular geometries that agree with the experimental structures in the cases of disulfur dinitride,  $S_2N_2$  ( $D_{2h}$  ground state)<sup>7</sup>, tetrasulfur tetranitride,  $S_4N_4$ <sup>8</sup>, the pentasulfur pentanitrogen cation,  $S_5N_5^{+9}$ , and the  $S_3N_3^-$ , the trisulfur trinitrogen cation<sup>3</sup>. In general, the MNDO calculated enthalpies of formation tend to be somewhat more negative than the corresponding experimental values for carbon containing compounds and the same is probably true for sulfur-nitrogen compounds as well. Nevertheless, in an absolute sense the values calculated are comparable in accuracy to those obtainable from minimal basis set, single determinant SCF calculations<sup>10</sup>. More importantly the values calculated relative to each other are probably reliable. Thus in the Table we indicate the enthalpy of formation of the materials listed relative to the enthalpy of formation of  $S_4N_4$ . It is somewhat difficult to assign absolute error estimates for the calculated heats of formation, but we estimate the values to be accurate to about 10%.

The unstable nature of these materials (note all the calculated  $\Delta H_f^\circ$ 's are positive) makes the experimental calorimetric measurement of heats of reaction for these materials difficult. The lack of knowledge of heat capacity data additionally complicates the experimental problem. Simple combustion calorimetry is complicated by the formation of gaseous products, i.e.,  $\text{SO}_3$  and  $\text{NO}_2$  and should probably be carried out in the presence of water to enable the formation of nitric and sulfuric acids. Until these problems are resolved it is hoped that these MNDO estimates of the standard enthalpies of formation will serve some useful purpose.

TABLE 1. Thermodynamic Data for Various Sulfur Nitrogen Compounds

| Compound                                     | $\Delta H_f^\circ$ (Kcal/mol) | I.P. (ev) | $\Delta H_f^\circ$ /relative <sup>†</sup> | Dipole Moment <sup>††</sup> |
|--|-------------------------------|-----------|---|-----------------------------|
| SNN  | 47.6                          | 10.4      | 0.237                                     | 1.57                        |
| NSN  | 212                           | 10.6      | 1.05                                      | 1.69                        |
| S <sub>2</sub> N <sub>2</sub>                | 118                           | 10.9      | 0.587                                     | 0.01                        |
| S <sub>2</sub> N <sub>2</sub> chain          | 147 <sup>*</sup>              | -         | 0.731                                     | 2.74                        |
|  | 142 <sup>**</sup>             | -         | 0.706                                     | 2.48                        |
| S <sub>2</sub> N <sub>2</sub> <sup>2+</sup>  | 771                           | 25.1      | 3.84                                      | -                           |
| S <sub>2</sub> N <sub>2</sub> <sup>2-</sup>  | 174                           | - 4.6     | 0.866                                     | -                           |
| S <sub>2</sub> N <sub>3</sub> <sup>1+</sup>  | 300                           | 18.2      | 1.49                                      | -                           |
| S <sub>3</sub> N <sub>2</sub> <sup>1+</sup>  | 309                           | 12.0      | 1.54                                      | -                           |
| S <sub>3</sub> N <sub>2</sub> <sup>2+</sup>  | 661                           | 23.4      | 3.29                                      | -                           |
| S <sub>3</sub> N <sub>3</sub> <sup>1-</sup>  | 89.7                          | 3.3       | 0.446                                     | -                           |
| S <sub>3</sub> N <sub>3</sub> <sup>1+</sup>  | 373                           | 15.3      | 1.85                                      | -                           |
| S <sub>4</sub> N <sub>3</sub> <sup>1-</sup>  | 10.1                          | 4.32      | 0.0502                                    | -                           |
| 1,2 S <sub>4</sub> N <sub>2</sub>            | 43.7                          | 10.8      | 0.217                                     | 1.67                        |
| 1,3 S <sub>4</sub> N <sub>2</sub>            | 104                           | 9.9       | 0.517                                     | 2.04                        |
| 1,4 S <sub>4</sub> N <sub>2</sub>            | 113                           | 9.8       | 0.562                                     | 1.62                        |
| S <sub>4</sub> N <sub>3</sub> <sup>1+</sup>  | 351                           | 14.6      | 1.75                                      | -                           |
| S <sub>4</sub> N <sub>4</sub>                | 201                           | 9.4       | 1.00                                      | 5.52                        |
| S <sub>4</sub> N <sub>4</sub> chain          | 236 <sup>*</sup>              | 9.56      | 1.17                                      | 0.81                        |
|  | 240 <sup>**</sup>             | 5.30      | 1.19                                      | 1.42                        |
| S <sub>4</sub> N <sub>4</sub> H <sub>4</sub> | 66.5                          | 10.1      | 0.331                                     | 1.54                        |

TABLE 1 (Continued)

| Compound                | $\Delta H^\circ_f$ (Kcal/mol) | I.P. (ev) | $\Delta H^\circ_f$ /relative <sup>+</sup> | Dipole Moment <sup>++</sup> |
|-------------------------|-------------------------------|-----------|---|-----------------------------|
| $S_4N_4^{2+}$           | 674                           | 19.8      | 3.35                                      | -                           |
| $S_4N_4^{2-}$           | 190                           | - 1.6     | 0.945                                     | -                           |
| $S_4N_5^{1+}$           | 389                           | 14.5      | 1.93                                      | -                           |
| $S_4N_5^{1-}$           | 219                           | 4.8       | 1.09                                      | -                           |
| $S_5N_5^{1+}$           | 434                           | 12.9      | 2.16                                      | -                           |
| $S_5N_5^{1+}$ (heart)   | 434                           | 12.9      | 2.16                                      | -                           |
| $S_5N_5^{1+}$ (azulene) | 434                           | 12.9      | 2.16                                      | -                           |

<sup>+</sup> The standard enthalpy of formation relative to  $\Delta H^\circ_f$  for  $S_4N_4$

<sup>++</sup> units - Debyes

\* (singlet state)

\*\* (triplet state)

# REFERENCES

1. For recent reviews see: Roesky, H. W., *Angew. Chem. Intl. Ed.*, 1979, 18, 91. Banister, A. J., *MTP. Int. Rev. Sci. Ser. 2, Inorg. Chem.*, 1975, 3, 41. Also, *Phos. and Sulfur*, 1979, 6, 421. *ibid*, 1978, 5, 147. Glemser, O., *Z. Naturforsch*, 1976, 31B, 610.
2. Baker, C. K.; Cordes, A. W.; Margrave, J. L., *J. Phys. Chem.*, 1965, 69, 334.
3. See for example, Mortimer, F. S.; Turner, A. G., *Inorg. Chem.*, 1966, 5, 906. Adkins, R.; Dell, R.; Turner, A. G., *J. Mol. Struct.*, 1976, 31, 403. Adkins, R. R.; Turner, A. G., *J. Amer. Chem. Soc.*, 1978, 100, 1383. Bhattacharyya, A. A.; Battacharyya, A.; Turner, A. G., *Inorg. Chim. Acta*, 1980, 42, 69. *ibid* 1980, 45, L13. Bhattacharyya, A. A.; Bhattacharyya, A.; Adkins, R. R.; Turner, A. G.; *J. Amer. Chem. Soc.*, 1981, 103, 7458.
4. For  $N_2S$ ; recent work by Chivers et. al. indicates that  $N_2S$  may be the primary fragment lost in the thermal decomposition of  $(ph)_3P = NS_3N_3$ , Chivers, T.; Cordes, A. W.; Oakley, R. T.; Swepston, P. N., *Inorg. Chem.*, 1981, 20, 2376. For  $S_4N_4^{2-}$ ; the evidence for this ion is less direct. Both polarographic studies, Tweh, J. W.; Turner, A. G., *Inorg. Chim. Acta*, 1981, 48, 173, and ESR experiments indicate its possible existence, Meinyer, R. A.; Pratt, D. W.; Myers, R. J., *J. Amer. Chem. Soc.*, 1969, 91, 6623. For  $S_2N_2$  open chain; this is a likely intermediate in the polymerization of disulfur dinitride to polysulfur nitride. Yamabe, T.; Tanaka, K.; Fukui, K.; Kato, H., *J. Phys. Chem.*, 1977, 81, 727.
5. Dewar, M.J.S.; Thiel, W., *J. Amer. Chem. Soc.*, 1977, 99, 4899. Bingham, R.; Dewar, M.J.S.; Lo, D. H., *ibid*, 1975, 97, 1285, 1294, 1302, 1307.

6. Pople, J. A.; Nesbet, R. K., Chem. Phys., 1951, 23, 69.
7. Adkins, R.; Dell, R.; Turner, A. G., J. Mol. Struct., 1976, 31, 403.
8. The structure calculated for  $S_4N_4$  in formation of the Table is in reasonable agreement with the x-ray studies.  $d_{N-S} = 1.60$ ; (exptl = 1.61), NSN angle =  $108^\circ$ , (exptl  $104^\circ$ ), SNN angle =  $120^\circ$ , (exptl =  $113^\circ$ ).
9. Gleiter, R.; Bartetzko, R., Z. Naturforsch. in press.
10. Kollmar, H.; Carrion, F.; Dewar, M.J.S.; Bingham, R. C., J. Amer. Chem. Soc., 1981, 103, 5295.